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of Hydrogen Peroxide.

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[REPRINTED FROM THE JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
VOL. XXIX, No. 9, SEPTEMBER, 1907].

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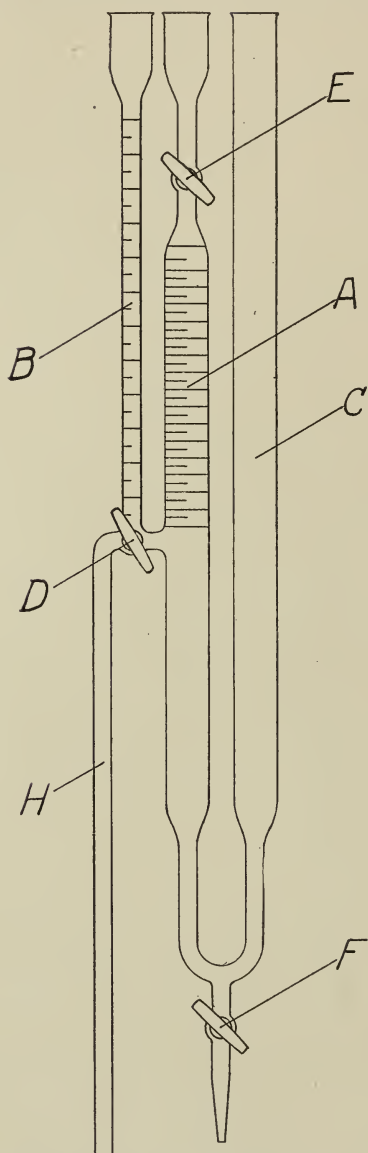
**A GASOMETRIC METHOD FOR THE DETERMINATION OF
HYDROGEN PEROXIDE.**

BY WILLIAM M. DEHN.

Received June 18, 1907.

The apparatus depicted in the figure was designed as an ureometer; its construction and the application to this purpose are described in another

contribution¹. It has been found that this instrument can be used also



for rapid and accurate determination of hydrogen peroxide. The reaction involved—

$\text{H}_2\text{O}_2 + \text{NaBrO} = \text{NaBr} + \text{H}_2\text{O} + \text{O}_2$ is immediate² and, as shown below, is sharply quantitative.

Method.—The stopcock E is opened and the stopcocks D and F are

¹ Z. anal. Chem. 45, 604.

² Lunge, Ber. 19, 1886; Tanatar, Ber. 32, 1013; Forester, J. pr. Chem. 63, 141.

closed, then the solution of sodium hypobromite¹ is poured in at the top of C until it fills the tubes A and C to some point above the stopcock E. The stopcock E is then closed and the stopcock F is opened so that the hypobromite in C may run down to the constricted portion—the hypobromite in A is then sustained by atmospheric pressure. The stopcock D² is turned from the position shown in the figure and is so controlled that B may first be washed with a little of the hydrogen peroxide and then be filled with the same to a readable height on the scale. Upon turning D so as to admit a regulated volume of the hydrogen peroxide solution, an immediate evolution of oxygen results. After admitting most of the hypobromite held above E, and letting stand for a minute or two so as to drain properly, the columns of hypobromite in A and C are brought to the same level, the volume of oxygen is read, and its weight and that of the corresponding hydrogen peroxide are calculated by the usual formulas.

A sample of hydrogen peroxide, whose specific gravity at 19° was 1.0133, gave by decomposition with a sodium hypobromite solution the following data :

Experiment	Vol. H ₂ O ₂	Vol. O ₂	Temperature	Atmospheric Pressure	Vapor Pressure NaBrO	Weight O ₂	Per Cent. H ₂ O ₂
1	5 cc.	11.40	26.8	742.2	19.75	0.01411	2.621
2	"	11.43	"	"	"	0.01414	2.628
3	"	11.37	"	"	"	0.01408	2.614
Average	"	11.40	"	"	"	0.01411	2.621
The same sample by the iodide titration method						=	2.625
" " " permanganate "						=	2.641

Other samples of hydrogen peroxide gave by this gasometric method results that coincided with the most careful analysis by the iodine titration method.

For most accurate analysis the vapor-pressures of the hypobromite solution used must be taken into account. The usual solution of hypobromite (sp. gr. 1.25) was found to exert the following vapor-pressures :

Temperature	Vapor-Pressure.		Difference
	NaBrO	H ₂ O	
4	1.1 mm.	6.1 mm.	5.0 mm.
8	1.8	8.0	6.2
12	3.3	10.5	7.2
16	5.3	13.6	8.3
20	8.6	17.4	8.8
24	12.8	22.2	9.4
28	18.0	28.1	10.1
32	24.0	35.4	11.4
36	29.5	44.2	14.7
40	36.0	55.0	19.0

¹ The usual method of preparation of this solution is as follows: dissolve 100 g. of caustic soda in 250 cc. of water and to each 100 cc. of this solution add 10 cc. of bromine and finally to the resulting solution add an equal volume of water. The specific gravity of the solution is 1.25. It need not be freshly prepared, nor is its efficiency rapidly impaired by repeated use. However it must be remembered that on diluting its vapor-pressure is increased and, by neglect of the same, errors approaching 1 per cent. may be introduced.

² This stopcock is ground or plugged so as to deliver only in the two directions of a right angle triangle.

Weight in milligrams of H_2O_2 corresponding to one cubic centimeter of moist oxygen.

$d/mm.$	728	732	736	740	744	748	752	756	760	764	768
4°	1.2664	1.2734	1.2802	1.2872	1.2942	1.3011	1.3081	1.3151	1.3222	1.3290	1.3359
8	1.2463	1.2531	1.2600	1.2669	1.2736	1.2805	1.2876	1.2944	1.3014	1.3081	1.3150
12	1.2251	1.2317	1.2387	1.2454	1.2522	1.2589	1.2657	1.2726	1.2823	1.2860	1.2928
16	1.2044	1.2111	1.2178	1.2245	1.2311	1.2378	1.2444	1.2512	1.2578	1.2646	1.2713
20	1.1817	1.1884	1.1948	1.2015	1.2080	1.2145	1.2213	1.2279	1.2345	1.2410	1.2475
24	1.1583	1.1649	1.1719	1.1777	1.1843	1.1907	1.1972	1.2036	1.2100	1.2169	1.2230
28	1.1345	1.1411	1.1476	1.1538	1.1603	1.1665	1.1731	1.1796	1.1857	1.1922	1.1986
32	1.1085	1.1149	1.1213	1.1275	1.1338	1.1401	1.1465	1.1528	1.1589	1.1652	1.1715
36	1.0843	1.0905	1.0967	1.1030	1.1093	1.1155	1.1214	1.1279	1.1341	1.1402	1.1465
40	1.0605	1.0666	1.0725	1.0786	1.0849	1.0909	1.0971	1.1033	1.1094	1.1155	1.1216

Here the vapor-pressures of the hypobromite solution are seen to be considerably less than the pressures of pure water. The effect of *different concentrations* of hypobromite may be seen in the following table :

NaBr Solution	H ₂ O added	Specific Gravity	Vapor Pressure	Difference H ₂ O
I	0	1.253	10.70	9.56
I	1	1.131	12.77	7.49
I	3	1.062	15.73	4.53
I	7	1.033	17.50	2.76
I	∞	1.000	20.26	0.00

In the preceding table, (p. 1318) cubic centimeters of oxygen under various conditions of temperature and pressure are calculated to milligrams of hydrogen peroxide, corrections for the aqueous pressure of the hypobromite (sp. gr. 1.25) and the effect of temperature on the barometric column are included.

By the use of this new gasometer, this hypobromite method and the table for calculating, the determination of hydrogen peroxide is made not only rapid and accurate but the necessity of preparing and correcting standard solutions is avoided and the presence of the usual preservatives in the peroxide solution can be neglected.

URBANA, ILL.
June 14th, 1907.



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